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Two-photonic photochemistry of NaBr in methanol solutions

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S1. Experimental details

Solutions were prepared from NaBr (Aldrich) and doubly distilled methanol (Merck). When necessary, the solutions were de-aerated by purging with argon. UV absorption spectra were recorded using Varian Cary 50 spectrophotometer (Varian Inc.). Laser flash photolysis setup (excitation at 266 nm, 5 ns pulse half-width, 1 – 15 mJ pulse energy) was used. The exciting laser beam was focused to a spot of 2 mm in diameter; laser energy flux was 40 – 400 mJ/cm^2. The probing beam of a xenon lamp was propagated under a small (ca. 2°) angle to the exciting beam. To determine the rate constants from experimental data, a system of differential equations corresponding to the selected reaction scheme was solved numerically by a fourth-order Runge-Kutta method, and the results were compared with the experimental kinetic curves.

S2. NaBr dissociation in methanol

The rate constant of NaBr dissociation in MeOH determined by Eq. S1 is 0.04 M [S1]. The calculated value of the ionic strength of NaBr solution $\mu = \frac{1}{2}\sum_i c_i z_i^2$ plotted *vs*. initial salt concentration is shown in Fig. S1.

$$\frac{[Na^+][Br^-]}{[NaBr]} = K_d \qquad (S1)$$

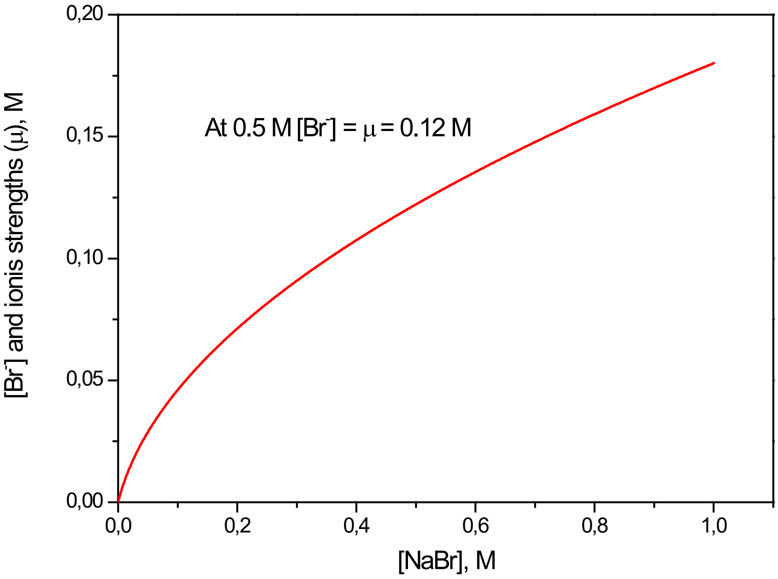

Figure S1. Ionic strength of NaBr solution in methanol *vs*. the initial NaBr concentration. Calculation with the dissociation constant $K_d = 0.04$ M [S1].

S3. Effect of the ionic strength on the rate constants of ionic reactions

The photochemical experiments were performed in methanol solutions with the large values of NaBr concentration, therefore, its influence on the rate constants of ionic reactions should be taken into account. The value of NaBr dissociation constant is $K_d = 0.04$ M [S1]. The dependence of the ionic strengths on the initial salt concentration is shown in Figure S1. The value of the ionic strengths at 0.5 M NaBr is 0.12 M.

The effect of ionic strength on the rate constant was evaluated using the Brønsted-Bjerrum theory combined with the extended Debye-Huckel theory (Equation S2, see Ref. [S2]).

$$f = lg\frac{k_\mu}{k_0} = \alpha\sqrt{\mu}\left[\frac{(Z_a+Z_b)^2}{1+d_{act}\beta\sqrt{\mu}} - \frac{Z_a^2}{1+d_a\beta\sqrt{\mu}} - \frac{Z_b^2}{1+d_b\beta\sqrt{\mu}}\right] \qquad (S2)$$

where d_a, d_b, d_{act} are average effective diameters of reacting ions and activated complex (in cm), Z_a and Z_b are ion charges, μ is ionic strength; ε is dielectric permeability (32.6 for CH_3OH), T is temperature (298 K), $\alpha = 1.825 \times 10^6 (\varepsilon T)^{-3/2}$ and $\beta = 5.03 \times 10^9 (\varepsilon T)^{-1/2}$.

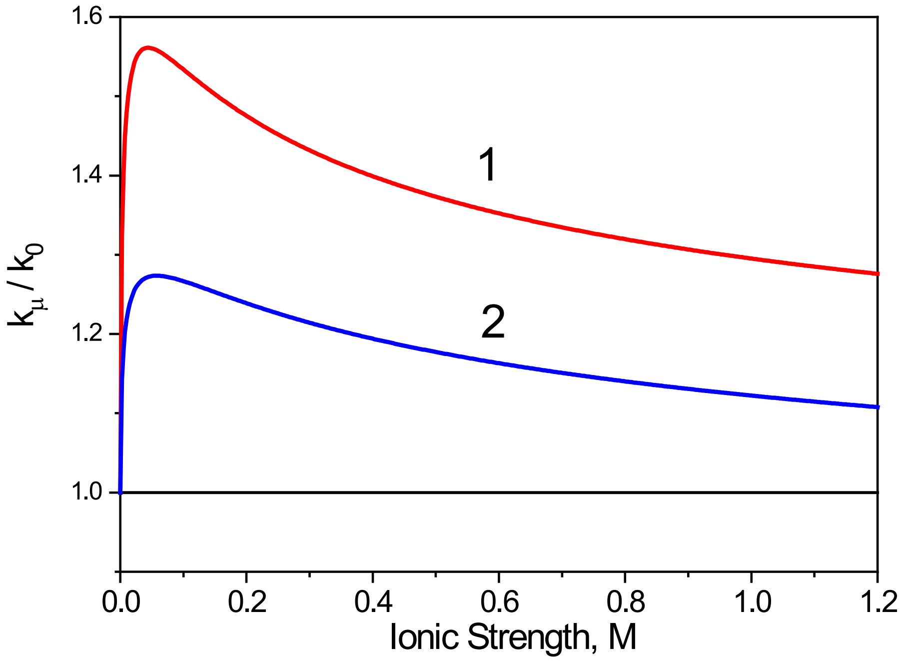

Figure S2. Effect of ionic strengths on the rate constants of ionic reactions. Calculated using Eq. S2. Curve *1* – reaction $Br_2^{\bullet-} + Br_2^{\bullet-}$ (with parameters: $d_a = d_b = 6.7$ Å, $d_{act} = 2d_a$), curve *2* – reaction $Br_2^{\bullet-} + O_2^{\bullet-}$ (with parameters $d_a = 6.7$ Å, $d_b = 3.5$ Å, $d_{act} = d_a + d_b = 10.2$ Å)

Results of the ionic strength effect on the rate constant of reaction ($Br_2^{\bullet-} + Br_2^{\bullet-}$) using Eq. S2 are shown in Fig. S3 (curve *1*). Parameters of calculation were: $d_a = d_b = 6.7$ Å [S3]; $d_{act} = 2d_a$. The dependence of rate constant of reaction ($Br_2^{\bullet-} + O_2^{\bullet-}$) was calculated in the same way and it is presented in Fig. S3 (curve *2*). Parameters of calculation were: $d_b = d_{O2} = 3.5$ Å (estimated based on internuclear distance and atomic radius of oxygen atom), $d_{act} = d_a + d_b = 10.2$ Å.

S5. Rate constants of the reactions considered in the paper

The numbering of the reactions corresponds to the main text of the paper.

$$\mathrm{Br^-} \xrightarrow[\mathrm{CH_3OH}]{2\,h\nu} \mathrm{Br^\bullet} + \mathrm{e^-_{solv}} \tag{1}$$

$$\mathrm{Br^\bullet} + \mathrm{Br^-} \xrightarrow{k_2} \mathrm{Br_2^{\bullet-}} \tag{2}$$

$$\mathrm{Br_2^{\bullet-}} + \mathrm{Br_2^{\bullet-}} \xrightarrow{2k_3} \mathrm{Br_3^-} + \mathrm{Br^-} \tag{3}$$

$$\mathrm{Br_2^{\bullet-}} + \mathrm{CH_3OH} \xrightarrow{k_4} {}^\bullet\mathrm{CH_2OH} + 2\,\mathrm{Br^-} + \mathrm{H^+} \tag{4}$$

$$\mathrm{Br_2^{\bullet-}} + \mathrm{e^-_{solv}} \xrightarrow{k_5} 2\,\mathrm{Br^-} \tag{5}$$

$$\mathrm{e^-_{solv}} + \mathrm{CH_3OH} \xrightarrow{k_6} \mathrm{CH_3O^-} + \mathrm{H^\bullet} \tag{6}$$

$$\mathrm{e^-_{solv}} + \mathrm{O_2} \xrightarrow{k_7} \mathrm{O_2^{\bullet-}} \tag{7}$$

$$\mathrm{Br_2^{\bullet-}} + \mathrm{O_2^{\bullet-}} \xrightarrow{k_8} 2\,\mathrm{Br^-} + \mathrm{O_2} \tag{8}$$

$$\mathrm{Br_2^{\bullet-}} + \mathrm{H^\bullet} \xrightarrow{k_9} 2\,\mathrm{Br^-} + \mathrm{H^+} \tag{9}$$

$$\mathrm{H^\bullet} + \mathrm{CH_3OH} \xrightarrow{k_{10}} {}^\bullet\mathrm{CH_2OH} + \mathrm{H_2} \tag{10}$$

$$\mathrm{H^\bullet} + \mathrm{O_2} \xrightarrow{k_{11}} \mathrm{HO_2^\bullet} \tag{11}$$

$$\mathrm{HO_2^\bullet} + \mathrm{Br_2^{\bullet-}} \xrightarrow{k_{12a}} 2\,\mathrm{Br^-} + \mathrm{H^+} + \mathrm{O_2} \tag{12a}$$

$$\mathrm{HO_2^\bullet} + \mathrm{Br_2^{\bullet-}} \xrightarrow{k_{12b}} \mathrm{Br_2} + \mathrm{HO_2^-} \tag{12b}$$

$$\mathrm{Br_2^{\bullet-}} + {}^\bullet\mathrm{CH_2OH} \xrightarrow{k_{13}} 2\,\mathrm{Br^-} + \mathrm{CH_2O} + \mathrm{H^+} \tag{13}$$

$${}^\bullet\mathrm{CH_2OH} + \mathrm{O_2} \xrightarrow{k_{14}} {}^\bullet\mathrm{OOCH_2OH} \tag{14}$$

$$2\,{}^\bullet\mathrm{OOCH_2OH} \xrightarrow{k_{15}} \text{products} \tag{15}$$

Table S1 Reactions followed by laser irradiation (266 nm) and their rate constants. μ - ionic strengths, important for ionic reactions (specified if available). If necessary, corrections to the value of ε_{max} ($Br_2^{\bullet-}$) = 9000 dm^3 mol^{-1} cm^{-1} were made.

Reaction	Rate constant, dm^3 mol^{-1} s^{-1}	Solvent, μ	Ref.	Lifetime*	Note
2	1.2×10^{10}	H_2O	[S4]	0.2 ns[+]	
	1.5×10^{10}	CH_3CN	[S5]		
3	$(5.5 \pm 0.5)\times10^{8}$	CH_3OH μ ~ 0.08 ÷ 0.2	[S6]	> 1 ms	Estimation from the experimental data
4	$(5.8 \pm 0.2)\times10^{2}$	CH_3OH	[S6]	70 μs	Estimation using $[CH_3OH]$ = 24.7 M
5	[^]1.0×10^{10}	H_2O μ ~ 0.1	[S7]	120 μs[+]	
6	$< 1\times10^{4}$	H_2O	[S8]	> 4 μs[+]	Estimation using $[CH_3OH]$ = 24.7 M
7	1.9×10^{10}	H_2O	[S9]	20 ns	Estimation using $[O_2] = 2.6\times10^{-3}$ M [S10]
8	1.9×10^{8}	H_2O μ ~ 0.1 $(0.5 \div 1.5)\times10^{-3}$	[S11]	~ 1 ms[+]	Dependence of rate constant vs. μ taken into account (see ESI)
9	1.4×10^{10}	H_2O	[S7]	15 μs[+]	
10	2.6×10^{6}	H_2O	[S9]	15 ns[+]	Estimation using $[CH_3OH]$ = 24.7 M
11	1.2×10^{10}	H_2O	[S9]	30 ns	Estimation using $[O_2] = 2.6\times10^{-3}$ M [S10]
12a	1.0×10^{8}	H_2O	[S11]	~ 4 ms[+]	Large scatter in the old experimental data
	1.6×10^{9}	H_2O	[S12]	300 μs[+]	
	4.6×10^{9}	H_2O	[S13]	100 μs[+]	
	6.5×10^{9}	H_2O	[S14]	70 μs[+]	
12b	9.7×10^{7}	H_2O	[S11]	~ 4 ms[+]	
13					No information; not sufficient in this work
14	4.2×10^{9}	H_2O	[S15]	90 ns	Estimation using $[O_2] = 2.6\times10^{-3}$ M [S10]
15	2.0×10^{8}	H_2O	[S16]	~ 2 ms[+]	Large scatter in the old experimental data
	1.1×10^{9}	H_2O	[S17]	~ 400 μs[+]	
	7.4×10^{8}	H_2O	[S18]	~ 600 μs[+]	

*Characteristic lifetime of the reaction at typical experimental conditions of this work (backward rate constant for the pseudo-first order reaction and half-time for the second order reactions).

[+] Estimation for CH_3OH taking the rate constant from other solvent.

[^] Corrected to the value of ε_{max} ($Br_2^{\bullet-}$).

S5. Photoionization of CH_3OH

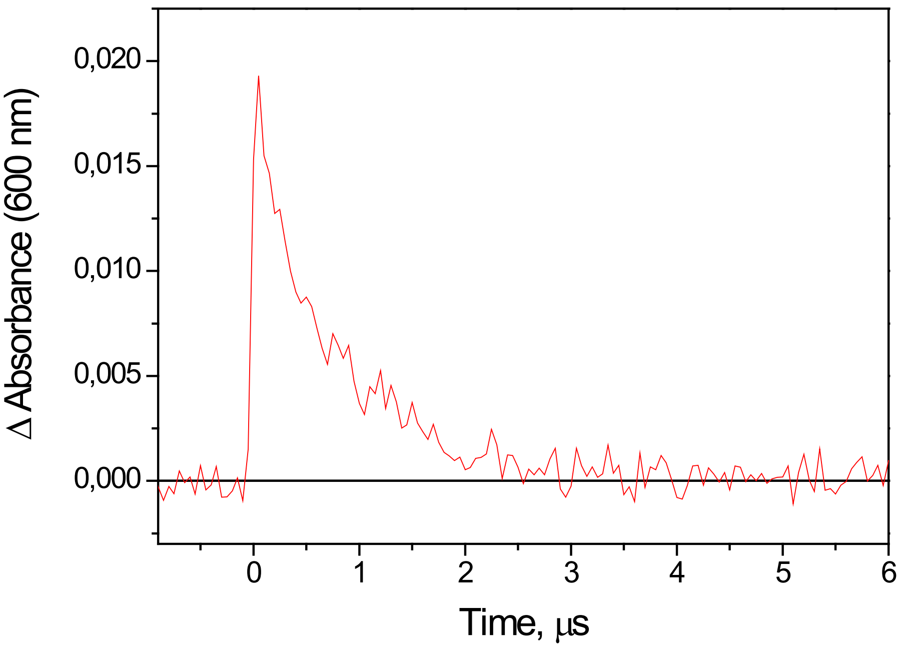

Figure S3. Kinetics of intermediate absorption (600 nm) of solvated electron caused by two-photonic excitation (266 nm) of neat methanol.

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